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# Role of Oxide Additives in Stabilizing Zirconia for Coating Applications

by Jeffrey J. Swab

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## **Role of Oxide Additives in Stabilizing Zirconia for Coating Applications**

**Jeffrey J. Swab**

Weapons and Materials Research Directorate, ARL

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## **Abstract**

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Zirconium dioxide ( $\text{ZrO}_2$ ) is a ceramic with a variety of industrial applications as a refractory material, and it is used in electronic packaging, biomedicine, and advanced engines. Unfortunately, pure zirconia undergoes a destructive phase transformation that severely limits its uses. However, some oxide additives have been found to control this transformation and ultimately lead to significant improvements in the material. This report summarizes the role that oxide additives play in controlling these transformations, and the resulting applications of  $\text{ZrO}_2$ -based coatings are discussed.

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# 1. Introduction

Zirconium dioxide ( $\text{ZrO}_2$ ) is a versatile ceramic material. Its high melting point (2,680 °C) makes it an ideal refractory material, and initially this was the extent of its industrial applications. Over the past several decades, however, significant advances have been made in understanding the processing/structure/properties relationships of zirconia. Extensive research was conducted on zirconia-based systems in the 1980s. In fact, during this time, there were three conferences specifically devoted to the science and technology of zirconia [1–3]. An advanced understanding of zirconia has led to its application as an oxygen sensor, thermally insulative and corrosion-resistant coating for advanced engines, a joint replacement material for human hips, and a variety of other high-temperature structural and wear applications.

Pure  $\text{ZrO}_2$  has severely limited applications due to a destructive tetragonal-to-monoclinic phase transformation. Fortunately, adding various oxides controls and enables the manipulation of this phase transformation. Through careful processing and compositional engineering, zirconia-based systems have been developed to satisfy the demands of many specialty applications. This report discusses the thermodynamic role of these oxide stabilizers in controlling the inherent phase transformations in  $\text{ZrO}_2$  and the application of  $\text{ZrO}_2$  coatings.

## 2. Zirconia Overview

**2.1 Phases.** Zirconia undergoes the following three solid polymorphic phase changes at atmospheric pressure:

Cubic  $\leftrightarrow$  Tetragonal  $\leftrightarrow$  Monoclinic.

The cubic (c-) phase, which is stable from 2,370 °C to the melting point, has a fluorite-type structure with each Zr atom octahedrally coordinated with eight oxygen atoms, all at an equal distance. Oxygen atoms are tetrahedrally coordinated to four equidistant Zr atoms. The

tetragonal (t-) phase is stable below 2,370 °C to approximately 1,170 °C. In this phase, the Zr atoms continue to be octahedrally coordinated to the oxygen atoms, but the eight oxygen atoms are no longer equidistant. Instead, four are approximately 15% closer to the Zr atoms than the other four oxygen atoms. This phase has a distorted crystal structure which is termed face-centered tetragonal. Monoclinic (m-)  $\text{ZrO}_2$  is stable at all temperatures below approximately 1,170°C. This is the naturally occurring mineral form of zirconia, baddeleyite, that also has a distorted tetragonal crystal structure. This phase is unique in that the Zr atoms have a sevenfold coordination with the oxygen at varying bond lengths and angles.

**2.2 Phase Transformations.** Pure  $\text{ZrO}_2$  undergoes two phase transformations after it cools from near the melting point to room temperature: (1) cubic to tetragonal ( $c \rightarrow t$ ), at approximately 2,370 °C and (2) tetragonal to monoclinic ( $t \rightarrow m$ ) around 1,170 °C. In both cases, the driving force for the transformation is so high (free energy of the t-phase  $[G_t] \gg$  the free energy of the c-phase  $[G_c]$  in the former, and the free energy of the m-phase  $[G_m] \gg G_t$  in the latter transformation) that it is thermodynamically impossible to retain either the c- or t-phase at room temperature, even with rapid quenching. The  $t \rightarrow m$  transformation is associated with a large crystallographic volume change which, even in small grains of pure  $\text{ZrO}_2$ , exceeds the elastic and fracture limits of the material and can only be accommodated by cracking and fracturing bulk pieces. This is the reason that large pieces of pure  $\text{ZrO}_2$  cannot be successfully manufactured.

Both of these transformations are diffusionless and have been termed “martensitic” since they are analogous to classic martensitic transformations that are common in many hardened steel systems. Although the control of both inherent phase transformations is of interest, the  $t \leftrightarrow m$  transformation has the greatest implications on the industrial application of zirconia and has thus been studied extensively. This transformation has five distinct features:

- (1) It is a diffusionless transformation in which the atoms retain their neighbors in either phase, and the atomic movements are small, occurring mainly with the oxygen atoms.

- (2) It involves a large shear strain ( $\approx 8\%$ ) and significant volume change (3–5%).
- (3) It exhibits a thermal hysteresis, with the forward transformation occurring around 1,170 °C and the reverse between 600 °C and 1,000 °C.
- (4) The t-phase cannot be retained at room temperature, even with rapid quenching.
- (5) The transformation is athermal (i.e., the amount of the transformed phase changes by varying the temperature, but not as a function of time at temperature).

A variety of oxide additives can successfully retain the c- and/or t-phase metastably at room temperature. In 1975, Garvie et al. [4] first proposed that the volume expansion associated with  $t \rightarrow m$  transformation could be beneficial in improving both the toughness and strength of ceramics. In these materials, the t-phase is retained metastably at room temperature by adding an oxide. The oxide acts to “stabilize” the  $\text{ZrO}_2$  structure by decreasing the transformation  $\Delta G$  and making it possible to retain the t-phase metastably at room temperature, avoiding the deleterious volume change.

The following sections will discuss the role of various oxides in the stabilization process, the resultant structure and properties of these materials, and the development of zirconia coatings.

### 3. Oxide Additives as Phase Stabilizers

**3.1 Selecting an Oxide Additive.** It has been known for years that adding certain oxides to  $\text{ZrO}_2$  will stabilize  $\text{ZrO}_2$  against its inherent phase transformations. Though the mechanisms by which these oxides serve to stabilize  $\text{ZrO}_2$  have been studied, there is still a lot to understand, and discussions continue as to the actual mechanisms. Research has, however, lead to the agreement of some general criteria for selecting stabilizing oxides. These four criteria are: 1) the cation radii should be close to that of  $\text{Zr}^{+4}$  (0.084 nm) to minimize lattice distortions which can lead to

high shear stresses and spontaneous transformations; 2) the cation should have a stable +2 or +3 state, which, when added to the  $\text{ZrO}_2$ , will produce oxygen vacancies; 3) the oxide crystal structure should be cubic or tetragonal, depending on the  $\text{ZrO}_2$  phase to be stabilized; and 4) the oxide should have some degree of solubility in  $\text{ZrO}_2$ , with a higher solubility preferred. These rules hold quite well. The one known exception to this,  $\text{CeO}_2$  ( $\text{Ce}^{+4}$ ), is an excellent stabilizing oxide, even though oxygen vacancies are not developed. The traditional oxide additives that have been used are  $\text{MgO}$  [5–7],  $\text{CaO}$  [7–9], and  $\text{Y}_2\text{O}_3$  [10–12]. A variety of commercial products based on  $\text{ZrO}_2$  have been produced using these additives. More recently,  $\text{CeO}_2$  [13–14] and other rare-earth oxides [15–20] have also been shown to stabilize  $\text{ZrO}_2$  to varying degrees. However, a major limitation to commercializing these rare-earth stabilized zirconias is the high cost of the oxide additive.

**3.2 Phase Relations in  $\text{ZrO}_2$ /Oxide Binary Systems.** The amount of added oxide, as well its solubility in  $\text{ZrO}_2$ , will determine the extent of stabilization and which phase and/or phases can be retained at room temperature. This section will review the binary phase diagrams of  $\text{ZrO}_2$  with the most common oxide stabilizers, as well as some of the newer rare-earth oxides.

**3.2.1  $\text{MgO-ZrO}_2$ .** There is still a lot of discussion on the exact phase diagram for the  $\text{MgO-ZrO}_2$  system, but the generally accepted diagram [6] is shown in Figure 1. In this system, there is little or no solubility of  $\text{MgO}$  in m- $\text{ZrO}_2$ . Between 1,240 °C and 1,400 °C, the solubility increases slightly to around 1 mole-percent in a tetragonal solid solution field. Above this temperature range, a large cubic solid solution field is present with a eutectoid composition at 13 mole-percent  $\text{MgO}$ . At this eutectoid composition, fully-stabilized cubic  $\text{ZrO}_2$  can be easily retained to room temperature with appropriate cooling. Most commercial materials are produced with a  $\text{MgO}$  content between 8 and 10 mole-percent, which results in a product with both c- and t-phases. It is beneficial to retain the t-phase since it can transform to the m-phase with the associated volume change and enhance the material's strength and toughness. This type of material is labeled as a partially-stabilized zirconia (PSZ) [6]. At higher  $\text{MgO}$  contents, with the c-phase being predominant, the material is considered a fully-stabilized zirconia (FSZ).

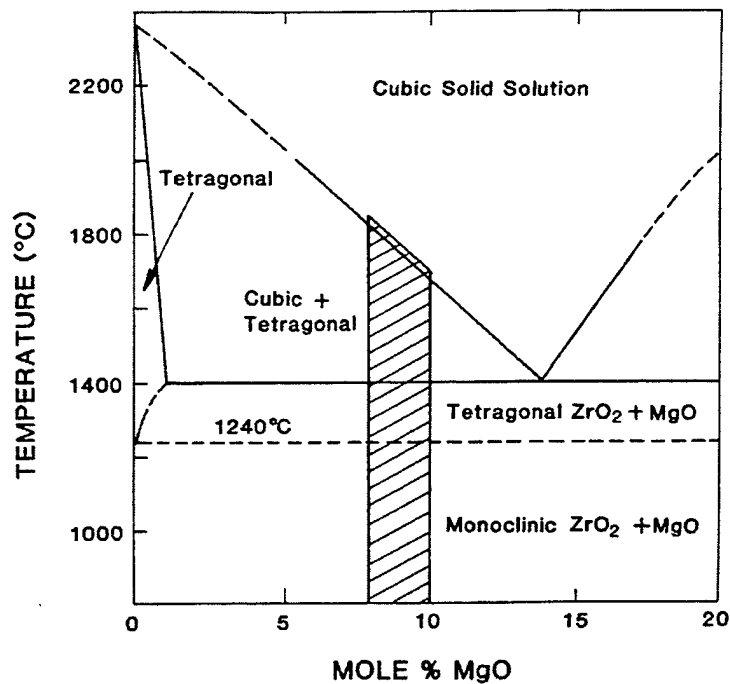


Figure 1.  $\text{ZrO}_2$ -Rich End of the  $\text{MgO}$ - $\text{ZrO}_2$  Phase Diagram [6].

Another feature of this system is the decomposition of the cubic solid solution to the other phases upon cooling. During decomposition, it is thought that the  $\text{MgO}$  leaves the  $\text{ZrO}_2$  and migrates along grain boundaries and to intergranular voids. The resultant  $\text{ZrO}_2$ , no longer properly stabilized, has inferior properties limiting its high temperature applications. Materials with low  $\text{MgO}$  content are very susceptible to large losses in strength and toughness when exposed to elevated temperatures ( $\sim 1,000^\circ\text{C}$ ) for long periods of time ( $>1,000$  hr) [21]. This “overaging” severely limits the high temperature applicability of this material.

**3.2.2  $\text{CaO}$ - $\text{ZrO}_2$ .** As with the  $\text{MgO}$ - $\text{ZrO}_2$  system, there is confusion about which phases are present, their compositions, and the eutectoid temperature. The most recent phase diagram is presented in Figure 2 [22]. Unlike the  $\text{MgO}$ - $\text{ZrO}_2$  system,  $\text{CaO}$  does exhibit solubility, albeit limited, in the m-phase below  $1,000^\circ\text{C}$ . At this low  $\text{CaO}$  content, increasing the temperature



Above 1,140 °C, with increasing CaO content, a two-phase region of tetragonal and cubic solid solution exists, and with further increases in CaO to ~20 mole-percent, a cubic solid solution phase exists. Slow cooling through the eutectoid at 1,140 °C at 17 mole-percent CaO results in a region with a tetragonal solid solution and a decomposition product. Both PSZ and FSZ materials can be produced in this system. However, the high temperature engineering applications of CaO-PSZ are limited because studies have shown that “aging” (time at temperature [ $>800$  °C]) results in microstructural changes that degrade the properties of the material [23].

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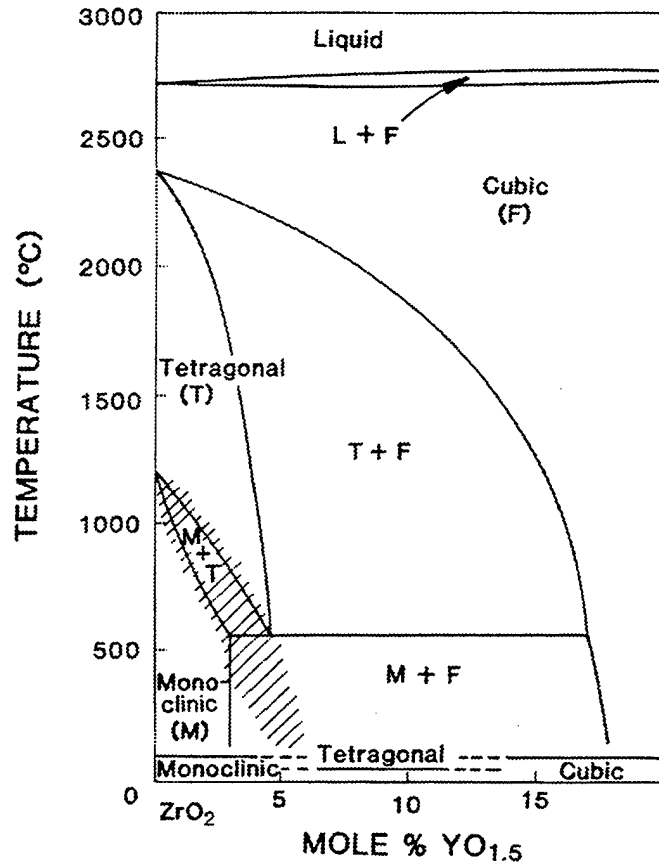


Figure 3. Low  $\text{Y}_2\text{O}_3$  Region of the  $\text{Y}_2\text{O}_3$ - $\text{ZrO}_2$  Phase Diagram [10].

transformation temperature is significantly lower. These two features enable the production of  $\text{ZrO}_2$  ceramics that are essentially 100% tetragonal phase with significantly improved strength and fracture toughness. These materials have been labeled as TZPs—tetragonal zirconia polycrystals.

Other features of this system are that two types of t- $\text{ZrO}_2$  can be developed. At  $\text{Y}_2\text{O}_3$  contents of approximately 4 mole-percent or less with increasing temperatures, a “transformable” t-phase field is encountered. This t-phase will transform to the m-phase on cooling. At  $\text{Y}_2\text{O}_3$  contents above 4 mole-percent, a mixture of c-phase and an “untransformable” t-phase, labeled as t'-phase, can be displacively created.

Because of the enhanced strength and toughness of  $\text{ZrO}_2$  with  $\text{Y}_2\text{O}_3$  contents between 2 and 4 mole-percent, the material has been examined for high-temperature structural applications, such as engine components [21, 24, 25]. Further additions of  $\text{Y}_2\text{O}_3$  create a homogeneous c-phase that is stable from room temperature to the melting point.

One drawback of this system is a well-documented, low-temperature aging phenomenon when the  $\text{Y}_2\text{O}_3$  content is below 4 mole-percent. At temperatures between 200 °C and 300 °C, and in the presence of water vapor, this material can undergo a catastrophic microcracking that can turn a bulk piece of  $\text{Y}_2\text{O}_3\text{-ZrO}_2$  to rubble [26–29]. Materials surviving intact have extensive microcracking that significantly reduces the properties and makes the material essentially useless.

There are many theories as to the cause of this phenomenon. Sato et al. [27] have proposed a theory where Zr-OH bonds are formed when water reacts with Zr-O-Zr bonds at the crack tip. They showed that in addition to aqueous solutions, certain nonaqueous solutions with a lone-pair electron orbital opposite a proton donor site enhance the rate of transformation at low temperatures. It was concluded that under these conditions, the strain that acts to stabilize the t-phase is released. This, coupled with the growth of pre-existing flaws, accelerates the transformation. The hypotheses of Yoshimura et al. [30–31] is similar in that it is also based on the formation of Zr-OH bonds, but they suggest a four-step degradation process. The  $\text{H}_2\text{O}$  is absorbed onto the Y-TZP surface and dissociates, forming Zr-OH bonds which create stress sites. These sites build as the  $\text{OH}^-$  ions diffuse through the surface and the lattice, resulting in “nucleation” sites for the phase transformation. When the stress level reaches a critical level, the  $t \rightarrow m$  transformation will occur with its associated cracking, enabling the process to continue. Their assumptions are based on findings which show that a transformed m- $\text{ZrO}_2$  had an OH group not found attached to untransformed t- $\text{ZrO}_2$ . Adding OH to the m-phase increases the lattice parameter, which can be returned to its original value if the specimen is dried.



Lange et al. [32] have seen the formation of 20–50 nm crystallites of  $\alpha\text{-Y}(\text{OH})_3$ , and they proposed that the formation of this hydroxide draws the yttria from the t-grains on the surface, creating monoclinic nuclei. As yttria depletion continues, these nuclei grow until a critical size is reached where they can spontaneously transform. If the transformed grains are large enough, microcracking will occur. The microcracking provides an avenue for the water to penetrate below the surface, which allows the process to continue. If the transformed grains are smaller than the critical size necessary for microcracking, the transformation and subsequent degradation will be limited by the long-range diffusion of  $\text{Y}_2\text{O}_3$  to the surface. Auger electron spectroscopy has shown a homogeneous, yttrium-rich surface layer on specimens after only 5 hr of exposure to 177 °C in a nitrogen environment [33]. This supports the theory of Lange et al. [32].

At low  $\text{Y}_2\text{O}_3$  levels, the grain size is critical. Lange reported that retaining the t-phase during processing depends on a combination of grain size and yttria content [34]. A critical grain size ( $D_c$ ) for retaining >90% of the t-phase can be defined by plotting the grain size vs. mole-percent yttria. The general trend is that as the amount of yttria is decreased, so must  $D_c$ . For a given yttria content above  $D_c$ , the retaining the t-phase becomes increasingly difficult. The same relationship seems to apply to this low-temperature degradation phenomenon [29], which has lead to the investigation of  $\text{CeO}_2$  and other rare-earth oxides as alternate stabilizers for  $\text{ZrO}_2$ .

**3.2.4  $\text{CeO}_2\text{-ZrO}_2$**  Like the  $\text{Y}_2\text{O}_3\text{-ZrO}_2$  system, this binary system exhibits an extensive tetragonal solid solution phase field, as shown in Figure 4 [35], giving rise to the formation of a TZP material. Unfortunately, the strength of this material is inferior to its  $\text{Y}_2\text{O}_3$  counterpart because the grain size is significantly larger. Although the commercial applications do not match those of the  $\text{Y}_2\text{O}_3\text{-ZrO}_2$  material, plasma-sprayed  $\text{CeO}_2$ -stabilized  $\text{ZrO}_2$  has been patented as a corrosion-resistant coating for superalloys [36].

**3.2.5 Other Rare-Earth Oxide- $\text{ZrO}_2$**  There have been several studies to examine other rare-earth oxides as stabilizers for  $\text{ZrO}_2$  [15–20]. Unfortunately, little research has focused on developing phase diagrams for these systems or on the resultant properties, so there are many questions yet to be answered.

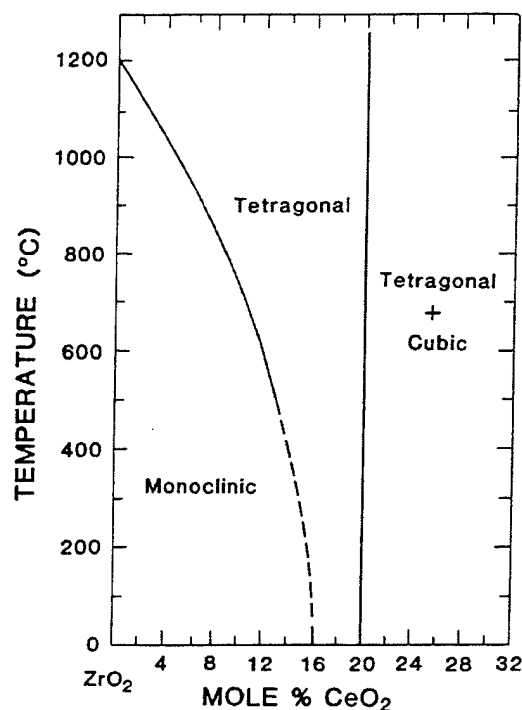


Figure 4. Low CeO<sub>2</sub> Region of the CeO<sub>2</sub>-ZrO<sub>2</sub> Phase Diagram [30].

Several of the studies [15–17] have examined mixtures of many of these oxides [17], or have added or partially substituted a second oxide in a Y<sub>2</sub>O<sub>3</sub>- [15–16] or CeO<sub>2</sub>-ZrO<sub>2</sub> [15] system. There have been some interesting results. Pyda et al. [17] used a mixture that primarily contained CeO<sub>2</sub>, Ln<sub>2</sub>O<sub>3</sub>, and Nd<sub>2</sub>O<sub>3</sub>, plus minor amounts of many other rare-earth oxides. They were able to obtain a fine-grained TZP material with a 5–7 mole-percent of the oxide mixture. When 3 mole-percent or more of the oxide mixture was used, chemical segregation occurred. Two ordered phases, Ln<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> and Ce<sub>2</sub>Zr<sub>3</sub>O<sub>10</sub>, coexist with the t-phase, and the amount of these phases increases with increasing stabilizer content.

Duh et al. [15] used a 12 mole-percent CeO<sub>2</sub>-ZrO<sub>2</sub> system as their base material. They found that replacing 2 mole-percent of the CeO<sub>2</sub> with Y<sub>2</sub>O<sub>3</sub>, Sm<sub>2</sub>O<sub>3</sub>, Nd<sub>2</sub>O<sub>3</sub> or Dy<sub>2</sub>O<sub>3</sub> resulted in a finer-grained material that was essentially all t-phase, but there was a significant decrease in fracture toughness. They proposed that reduced fracture toughness was due to either reduced free energy

of the t-phase, or an increase in the constraint on the t-grains, preventing transformation. One unmentioned possibility was that these substitutions might result a nontransformable t-phase.

Log et al. [18] attempted to produce  $\text{ZrO}_2$  material using 3 mole-percent of a variety of rare-earth oxides in place of  $\text{Y}_2\text{O}_3$ . The purpose was to lower the annealing temperatures for a displacively formed t'-phase. They fabricated polycrystalline t'- $\text{ZrO}_2$  using  $\text{Dy}_2\text{O}_3$ ,  $\text{Er}_2\text{O}_3$ , and  $\text{Yb}_2\text{O}_3$ . The material had toughness values significantly higher than c- $\text{ZrO}_2$ , but the strength was severely reduced by the large grain size.

Another study investigating the development of zirconia fibers by sol-gel processing added different concentrations of a variety of rare-earth oxides [19]. The large cation radius of Ln, Pr, and Nd yielded t- $\text{ZrO}_2$  when calcined at 900 °C, but yielded partly or fully m- $\text{ZrO}_2$  with or without a cubic zirconia phosphate phase at higher temperatures. The smaller cation radius of Sm, Gd, and Dy yielded only t- $\text{ZrO}_2$  and c- $\text{ZrO}_2$ , or a combination of these two phases. The crystallite size, lattice strain, and tensile strength were also affected by this difference in cation size.

Duran [20] produced a phase diagram for the  $\text{Er}_2\text{O}_3$ - $\text{ZrO}_2$  binary system using high-temperature x-ray diffraction and thermal expansion measurements. He showed that erbia could indeed stabilize  $\text{ZrO}_2$ , but the effect on the properties of the resultant materials was not reported.

Jones [37–39] investigated other oxides for stabilizing  $\text{ZrO}_2$  for corrosion-resistant thermal barrier coatings (TBC) in engine applications.  $\text{Sc}_2\text{O}_3$  and  $\text{In}_2\text{O}_3$  have been examined because  $\text{Y}_2\text{O}_3$  can be effectively leached from the  $\text{ZrO}_2$  by some fuel impurities, resulting in the degradation of TBC. The phase relations in these systems have not been examined in great depth as part of these studies.

**3.3 Microstructures in  $\text{ZrO}_2$ /Oxide Binary Systems.** The most common, and thus most utilized microstructures that result from stabilizing  $\text{ZrO}_2$  by adding an oxide are described in the next section.

**3.3.1 Partially Stabilized Zirconia (PSZ).** PSZ materials are generally developed by adding  $\text{MgO}$ ,  $\text{CaO}$ , or  $\text{Y}_2\text{O}_3$  at levels that will allow c-phase to be formed without completely stabilizing the c-phase. These materials are heated in the c-phase field and when cooled t-grains precipitate out. At room temperature, the metastable t-phase, lenticular in shape, is confined in the c-matrix. The cooling portion is critical to the properties of the final product. The aim of cooling is to uniformly distribute the t-grains, retain as many of the precipitated grains in the t-phase at room temperature as possible, and avoid the precipitation of the t-grains at the grain boundaries, which can lead to the spontaneous transformation to m-grains.

This coarse-grained microstructure (grains are typically between 25 and 75  $\mu\text{m}$ ) is achieved by first rapidly cooling to below 1000  $^\circ\text{C}$  to produce the t-phase precipitates confined in the c-grains. The martensitic start ( $M_s$ ) temperature of the t-grains is below room temperature. If this rapid cooling is sustained far below 1000  $^\circ\text{C}$ , an “underaged” material will result; the size of the t-grains are so small that even under an applied stress they will not transform. Next, the t-grains must be coarsened to the critical size so that they will transform easily under an applied stress. If the coarsening is done for too long, the grains will grow beyond the critical size, the  $M_s$  temperature will be above room temperature, and the grains will spontaneously transform to the m-phase when cooled; this is termed “overaging.”

**3.3.2 Tetragonal Zirconia Polycrystals (TZP).** These are also partially stabilized zirconias, but the oxide additive and the resultant microstructure are quite different from the PSZ materials. TZPs are typically stabilized by adding  $\text{Y}_2\text{O}_3$  or  $\text{CeO}_2$  because the solubility of each in  $\text{ZrO}_2$  is much greater than either  $\text{MgO}$  or  $\text{CaO}$ . This enables greater stability of the t-grains against the  $t \rightarrow m$  transformation, allowing the production of a  $\text{ZrO}_2$  which is essentially 100% tetragonal. The t-grains are faceted and fine grained ( $\approx 2 \mu\text{m}$  or less, depending on the firing time,

temperature, and oxide content). Rühle and Heuer [40] indicated that autocatalytic nucleation is important for enhancing toughness in this class of zirconias. That is, the stress created by the t-grains that transform is transferred to neighboring grains, causing further transformation; thus, a discrete area of monoclinic grains surrounding the propagating crack tip are formed.

**3.3.3 Zirconia-Toughened Ceramics (ZTC).** Another class of partially stabilized zirconia systems are those in which  $\text{ZrO}_2$  is not the matrix material, but rather it is dispersed in the matrix to enhance toughness. These materials are commonly referred to as zirconia toughened ceramics (ZTC).

By far, the most common material is zirconia toughened alumina (ZTA). Initial efforts centered on adding unstabilized  $\text{ZrO}_2$  to  $\text{Al}_2\text{O}_3$ . Both t- and m-grains of  $\text{ZrO}_2$  toughened  $\text{Al}_2\text{O}_3$  through phase transformation and/or microcracking toughening. Toughening could only be achieved with less than a 20 volume-percent of unstabilized  $\text{ZrO}_2$ . The volume content of  $\text{ZrO}_2$  could be much higher if the  $\text{ZrO}_2$  was partially stabilized.  $\text{ZrO}_2$ , with small amounts (2–3 mole-percent) of  $\text{Y}_2\text{O}_3$  (TZP type) were added to  $\text{Al}_2\text{O}_3$ , resulting in significant improvements in strength and toughness [41, 42]. Other ZTC systems include zirconia toughened spinel [43] and mullite [44, 45]. Attempts have been made with varying degrees of success to combine  $\text{ZrO}_2$  (in a variety of forms) with nonoxides such as  $\text{Si}_3\text{N}_4$  [43, 46, 47],  $\text{SiC}$  [43, 48] and  $\text{TiB}_2$  [49].

## 4. Aspects of Toughening by $\text{ZrO}_2$

Controlling and manipulating both transformations, especially the t→m transformation, has lead to the development of a class of zirconia materials that are deemed “transformation toughened.” There are several subclasses of these materials, but in all cases, toughening occurs when the stress field in front of a propagating crack encounters a t-grain. If sufficiently large enough, this stress field can initiate the t → m transformation, thus increasing the material’s resistance to crack propagation. This section discusses some aspects of transformation toughening.

**4.1 Nucleation of Martensitic Transformations.** The kinetics of the  $t \rightarrow m$  transformation in  $\text{ZrO}_2$  are nucleation controlled and can be examined as a transformation in either an “unconfined” or a “confined” state. Single-crystal  $\text{ZrO}_2$  is the best material for examining the nucleation in an unconfined state, but PSZs, TZPs, and zirconia toughened ceramics, such as ZTA, where the  $t$ -grains are confined, is of greater industrial importance. Early discussions focused on whether this transformation followed a classical or a nonclassical model. Nucleation of the martensitic transformation in steels is considered a classic heterogeneous transformation since specific defect sites, typically dislocation based, serve as the nuclei for transformation.

Heuer and Rühle [40, 50] determined that the transformation in a confined state follows a nonclassical model. In all cases (PSZ, TZP, and ZTC), nucleation is the same, irrespective of whether it occurs on cooling during production, or in the presence of a stress field at the crack tip. The lack of dislocations in PSZ and ZTA are their reason. Some dislocations have been observed in TZPs, but they typically do not act as nucleation sites. Instead, the nucleation sites are particle/matrix interfaces or grain boundaries that act as a stress concentrator. They believe that nucleation is always stress-assisted, and that the stresses are typically produced during precipitation. Additionally, elastic moduli and thermal expansion mismatches, as well as thermal expansion anisotropy and crack tip stress, contribute to the overall stress at these nucleation sites. Particle size plays an important role in the nucleation and transformation of the  $t$ -phase.

**4.2 Effect of Particle Size.** Particle and grain size is critical to retaining the  $t$ -phase at room temperature in either an unconfined or confined state. Lange [51] determined that for a given temperature, there is a critical grain size necessary to prevent a spontaneous  $t \rightarrow m$  transformation during cooling. If the  $t$ -grains are below this critical size, the thermodynamic free energy for the transformation is high and few grains transform. However, when these grains are above the critical size, the free energy is lowered, and the  $t$ -grains can spontaneously transform. Finding the appropriate grain size is critical to applying the material and depends on the oxide additive, its content, and the production technique.

This critical size also applies to the transformation under an applied stress field, such as that in front of a propagating crack. For enhanced toughening, the ideal condition is for the t-grains to be a size just below the size necessary for spontaneous transformation. In PSZ materials, the size dependence is pronounced. The t-phase is present as coherent precipitates, with an oblate shape (which minimizes stresses), in a c-phase field. Proper “aging” (exposure to elevated temperatures) of PSZ can easily bring the precipitates to the edge of this critical size. It can also just as easily coarsen the grains beyond this critical size through “overaging,” resulting in a spontaneous transformation and the loss of toughening.

This is why TZP materials are of such interest. The fine-grained ( $\leq 1 \mu\text{m}$ ), essentially 100% t-phase is significantly less likely to suffer from overaging. The grain size is well below the critical size, minimizing the likelihood of spontaneous transformation. The fine grain size also enhances the material’s strength. Unfortunately, this fine grain size can also have an adverse effect on the fracture toughness. If these grains are too small, few will transform, even in the presence of the crack tip stress field. Since the transformation is inhibited, there is minimal contribution from the transformation, resulting in a low fracture toughness.

**4.3 Toughening Mechanisms in  $\text{ZrO}_2$  Systems.** In general, one of the major disadvantages of ceramics is that they are brittle—they have an inherent lack of toughness (resistance to crack propagation). Many attempts have been made, with varying degrees of success, to improve toughness in ceramics. These include compositional tailoring of the microstructure (in-situ toughening), or adding a second-phase material such as particulate, whiskers, fibers, or some combination. Many materials that are comprised of t-grains of  $\text{ZrO}_2$  or contain these grains have toughness values higher than most ceramics. The  $t \rightarrow m$  transformation is the reason for this enhancement. It is believed that there are three primary mechanisms: transformation toughening, microcrack toughening, and crack deflection [52, 53].

**4.3.1 Transformation Toughening.** This mechanism is a form of crack shielding. As a crack propagates, a zone of transformed grains develops in front of the crack tip. This zone reduces the stress at the crack tip, resulting in crack shielding and a resistance to crack extension.

If this zone not only extends in front of the crack tip, but also surrounds the crack (i.e., a wake), then a material may exhibit an R-curve effect (i.e., increasing toughness with increasing crack length). Many materials containing t-ZrO<sub>2</sub> exhibit this effect. This form of toughening is only expected when a wake develops during crack extension. In a material exhibiting an R-curve, it is easy for a small crack to propagate, and then the material becomes insensitive to the presence of large cracks.

**4.3.2 Microcrack Toughening.** This type of toughening occurs when an extending crack encounters a zone of microcracks. The microcracks significantly reduce the driving force for crack extension through crack bifurcation. Microcrack zones can arise in a material through localized residual stresses, which may be due to from thermal expansion, elastic modulus mismatches, or phase transformations. Low toughness grain boundaries may act as sites for developing such cracks. In materials comprised of or containing t-ZrO<sub>2</sub>, microcracking may occur during fabrication since some t-grains transform during cooling. Controlling the amount of microcracking is critical, as zones of microcracks can act as stress concentrators and lead to a strength reduction. In terms of enhancing fracture toughness, the ideal case is to develop a material in which the t-grains are below the critical size necessary for spontaneous transformation, but in a range where it is possible to induce the development of a microcrack zone. A zone of microcracks may also form in front of a propagating crack because of the phase transformation. In this case, microcrack toughening can be considered a form of crack shielding.

**4.3.3 Crack Deflection.** In this mechanism, the crack is deflected out of a plane normal to the maximum tensile stress field. This can be accomplished by adding a second-phase material, or it can be caused by localized residual stresses. This mechanism is not as dominant in zirconia systems as are transformation or microcrack toughening, and it is not sensitive to temperature increases. This is an attractive way to produce materials that have fracture toughness values that are not temperature dependent.



## 5. Developing ZrO<sub>2</sub> Coatings

Materials based on ZrO<sub>2</sub> have been examined for a variety of industrial applications. Monolithic PSZ and TZP materials, with their high strength and toughness, were examined for gas turbine and diesel engine components. However, these materials have not been able to find a niche in engines because of reduced  $t \rightarrow m$  driving force at elevated temperatures and the associated loss of properties and performance.

One area of the engine community in which zirconia is finding an application is as a thermally insulative coating (thermal barrier coating [TBC]), or as an environmental barrier coating (EBC). TBCs are used in many turbine engine applications to insulate a metallic component from high combustion temperatures; this leads to longer lifetimes for these components. An EBC the coating is designed to protect the metallic component from degradation due to corrosive media produced/ingested in the engine combustion cycle. In some cases, both thermal and environmental protection are necessary, and zirconia-based coatings are successfully being used to provide combined protection.

**5.1 Coating Deposition.** Zirconia coatings are typically deposited by a thermal spray process. Thermally deposited coatings are a cost-effective means of solving a variety of engineering problems. These types of coatings are most commonly applied to provide thermal insulation, improve wear, oxidation, or corrosion resistance, or to restore worn components. Thermal spraying is a term that describes a family of techniques that are used to deposit metallic or nonmetallic coatings onto prepared substrates. The spraying techniques (that are classified based on the heating source and the introduction of the coating material) include plasma, flame, wire arc, high-velocity oxyfuel (HVOF), and detonation gun. In all techniques, the coating material, in the form of a powder, rod, or wire, is melted by the heat source. Compressed air or a process gas accelerates a confined stream of these molten particles onto a substrate. On impact, the particles flatten, solidify, and form interlocking platelets that bond to the substrate. These techniques are similar to a welding, except that in welding the material is fused to the substrate

and stays attached through a metallurgical bond, while thermally sprayed coatings remain attached through a mechanical bond. Further details and information on the various thermal spray techniques can be obtained from references [54–57].

Plasma spraying is the preferred technique for depositing  $\text{ZrO}_2$ -based coatings. In this technique, an electric arc is used to heat a gas or gas mixture to temperatures approaching 10,000 K. The gas ionizes creating a plasma. The powder is injected into this plasma and melted. The molten particles are then accelerated toward the substrate at speeds approaching Mach II velocities. The temperature and velocity of this plasma stream is controlled by the nozzle design, arc current, gas flow rate, and gas mixture ratio. Excellent coatings with high bond strength are produced by this method, and the process flexibility allows for producing coatings with varying density and porosity levels.

**5.2 Thermal Barrier Coatings.** TBCs are used in many turbine engine applications to insulate metallic components from high combustion temperatures leading in longer lifetimes for these components. Kvernes and Fartum [58] in Norway and Kamo and Bryzik [59] in the United States were some of the first to pioneer the use of plasma-sprayed ceramics in diesel engines. These coatings can be considered for application on the following diesel engine components: cylinder liners, piston caps, and valve faces. Almost all TBCs for engine applications are plasma-sprayed  $\text{ZrO}_2$ -based materials. There are several reasons for using  $\text{ZrO}_2$ -based materials. These coatings have extremely low thermal conductivity values (typically around 2 W/m K) that are significantly lower than the thermal conductivity of the metallic component. The powders of these materials are readily available and easy to deposit as a coating via a variety of thermal spraying techniques. A coating of 2 mm or less of this highly insulative ceramic can result in an increase in the component life by several orders of magnitude. Also, the coating is cheaper than the component it coats.

A joint effort between the U.S. Army Tank and Automotive Command (TACOM) and Cummins Engine Co. in the early 1980s [60], led to the development of a prototype engine that

was placed in a military truck. The high temperature and thermal insulating properties of zirconia coatings were examined in an attempt to retain the maximum amount of heat content in the exhaust gas and reduce or eliminate engine cooling. (Approximately 50% of engine field failures, both commercial and military, were related to the cooling system.) This uncooled, low-heat rejection engine had the entire combustion area insulated with a thin zirconia coating. The engine was redesigned to have 361 fewer parts than the standard diesel engine. The omitted parts were mainly from the cooling system and included the radiator, fan, and water pump. Removal of these parts resulted in a  $0.56 \text{ m}^3$  ( $20 \text{ ft}^3$ ) decrease in engine volume and a reduction in the net weight of the engine by 153 kg (338 lb). Road testing of over 129,000 km (80,000 mi) showed an improvement in fuel economy of 50%, from 6 mpg to 9 mpg.

Since this early work, the use of TBCs has grown; the state-of-the-art coating material is  $\text{ZrO}_2$ , with a content between 6 and 12 weight-percent  $\text{Y}_2\text{O}_3$ . Adding this amount of  $\text{Y}_2\text{O}_3$  yields a fully-stabilized  $\text{ZrO}_2$  material that provided the necessary thermal insulation. Although these coatings showed great promise, there were barriers to their widespread use. One barrier was that the coating adhered poorly to the metal substrate, which limits the coating lifetime and durability. In an engine environment, a coating experiences severe thermal cycling. This thermal cycling resulted in the initiation and growth of thermal-shock-induced cracking at the coating/substrate interface, which ultimately leads to spallation of the coating and exposure of the underlying metal. This led to the development of a duplex coating system, where an MCrAlY (typically  $\text{M} = \text{Ni}$ ) bond coat ( $\approx 0.1 \text{ mm}$  thick) is deposited on the metal prior to depositing the TBC. This bond coat improves the adherence of the TBC and serves as an oxidation barrier for the metal. Other systems of multilayered coatings or functionally graded materials (FGMs) have also been examined with success [61–63].

**5.3 Environmental Barrier Coatings.** A long-range goal of the military is to develop engines that can handle alternate fuels (i.e., various grades of gasoline, diesel, and shale oil or coal-derived fuels) without requiring physical adjustment to the engine or compromising engine performance [64]. Low-grade fuels commonly contain parts per million of one or more of the

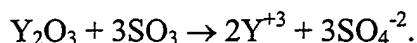
following: Na, S, K, and V. During the combustion process, reactions can occur involving these impurities, creating compounds that can corrode engine components.

Typically, corrosion is only a problem between the melting point and the dew point of the corrosive media, since in this temperature range the corrosive compounds are fluid and can rapidly spread, enhancing the corrosion process. Below the melting point, transport is too slow; thus, the corrosion rate is very limited. Above the dew point, thermodynamics inhibit the formation of the corrosive media due to evaporation. However, higher pressures increase the dew point and thus the temperature range in which corrosion is possible. Since advanced engines are expected to operate at higher temperatures and pressures it is important to understand how the various corrosive media affect T/EBC materials.

**5.3.1 Interaction of  $ZrO_2$  and Typical Corrosive Media.** How does  $ZrO_2$  and its stabilizing oxides react with typical corrosive media produced in an engine combustion process? This question must be answered to understand how to develop  $ZrO_2$ -based T/EBCs for engine applications. Zirconia stabilized with  $Y_2O_3$  or  $CeO_2$  are the materials typically used for engine applications. Some of the most common corrosive media are molten salts containing sulfur and/or vanadium.

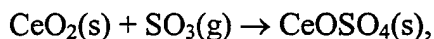
**5.3.2 Interaction of Zirconia and Its Stabilizing Oxides With Sulfur Compounds.** Molten salts containing Na are formed during engine combustion; they “leach” the cation ( $Y^{+3}$  or  $Ce^{+4}$ ) from the  $ZrO_2$ , causing surface destabilization and property degradation. This leaching phenomenon is analogous to the hypotheses proposed by Lange et al. [32] to account for the catastrophic degradation of Y-TZP materials that can occur at low temperatures in the presence of water vapor.

Barkalow and Petit [65] first proposed that yttrium is leached from a  $Y_2O_3$ -stabilized zirconia by the following sulfation reaction:



This reaction depends on the partial pressure of  $\text{SO}_3$ . A partial pressure increase in  $\text{SO}_3$  at elevated temperatures speeds the removal of yttrium. Later work confirmed the high reactivity of  $\text{Y}_2\text{O}_3$  with  $\text{SO}_3$  and yielded a similar reaction, but this work suggested  $\text{Y}_2\text{O}_2(\text{SO}_4)_3$  or  $\text{Y}_2(\text{SO}_4)_3$  as sulfation products [66]. These tests showed that  $\text{Y}_2\text{O}_3$  was so reactive, the equilibrium partial pressure of  $\text{SO}_3$  could not be measured at 700 °C.

Jones et al. [67] examined the sulfation of pure  $\text{CeO}_2$  and pure  $\text{ZrO}_2$ . They concluded that the sulfation of  $\text{CeO}_2$  followed the equation



at temperatures above 650 °C and combined with an  $\text{SO}_3$  pressure of 30 Pa and higher. The  $\text{ZrO}_2$  is difficult to sulfate. It remains essentially unsulfated at  $\text{SO}_x$  partial pressures of  $\approx 1000$  Pa at 700 °C. Therefore, the hot corrosion resistance of  $\text{ZrO}_2$  materials by  $\text{Na}_2\text{SO}_4$  depends on the stabilizer rather than the zirconia. The thermodynamic data indicate that  $\text{CeO}_2$ - $\text{ZrO}_2$  will be more resistant to corrosion by molten  $\text{Na}_2\text{SO}_4$  than the  $\text{Y}_2\text{O}_3$ - $\text{ZrO}_2$ . As previously mentioned, plasma-sprayed  $\text{CeO}_2$ - $\text{ZrO}_2$  has been patented as a corrosion-resistant coating for superalloys [36].

**5.3.3 Interaction of  $\text{ZrO}_2$  and Its Stabilizing Oxides With Vanadium Compounds.** Jones et al. [68] showed that the reaction between the vanadium-based corrosive media and ceramic oxides, such as  $\text{Y}_2\text{O}_3$ ,  $\text{CeO}_2$ , and  $\text{ZrO}_2$ , follows a Lewis acid-base mechanism. These oxide additives were reacted with  $\text{Na}_3\text{VO}_4$ ,  $\text{NaVO}_3$ , and  $\text{V}_2\text{O}_5$ . Table 1 summarizes these findings. None of the ceramic oxides reacted with  $\text{Na}_3\text{VO}_4$ . While  $\text{CeO}_2$  and  $\text{ZrO}_2$  did not react with  $\text{NaVO}_3$ ,  $\text{Y}_2\text{O}_3$  did react to form  $\text{YVO}_4$ .  $\text{YVO}_4$  was also the product when  $\text{Y}_2\text{O}_3$  reacted with  $\text{V}_2\text{O}_5$ , and  $\text{CeVO}_4$  when  $\text{CeO}_2$  reacted with  $\text{V}_2\text{O}_5$ .  $\text{ZrO}_2$  also exhibited some reactivity producing

Table 1. Reaction Behavior and Products for Ceramic Oxide-Vanadium Compounds [68].

		Increasing Acidity →		
Increasing Acidity ↓		$\text{Na}_3\text{VO}_4$	$\text{NaVO}_3$	$\text{V}_2\text{O}_5$
	$\text{Y}_2\text{O}_3$	NR <sup>a</sup>	$\text{YVO}_4$	$\text{YVO}_4$
	$\text{CeO}_2$	NR	NR	$\text{CeVO}_4$
	$\text{ZrO}_2$	NR	NR	$\text{ZrV}_2\text{O}_7$ (slowly)

<sup>a</sup>NR = No Reaction.

$\text{ZrV}_2\text{O}_7$ , but this reaction was extremely slow. Again, these findings show that the stabilizing cation can be leached from  $\text{ZrO}_2$ , and that the stabilizing oxide in  $\text{ZrO}_2$  will limit the materials' corrosion resistance. More importantly, however, the tendency to react is based on an acid-base relationship between the oxide and molten salt. The more acidic the ceramic oxide, the more corrosion resistant the material. Hence, research has begun to investigate oxides which were more acidic than either  $\text{Y}_2\text{O}_3$  or  $\text{CeO}_2$ .

**5.3.4 Scandium and Indium Oxides as Hot-Corrosion-Resistant Stabilizers for  $\text{ZrO}_2$ .** A review of other rare-earth oxides shows that 5 weight-percent of  $\text{Sc}_2\text{O}_3$  is effective in stabilizing t- $\text{ZrO}_2$  [69]. It also happens to be significantly more acidic than  $\text{Y}_2\text{O}_3$ . Studies have shown that  $\text{Sc}_2\text{O}_3$  essentially did not react with  $\text{NaVO}_3$  [37] or  $\text{V}_2\text{O}_5$  [39], even after hundreds of hours at elevated temperatures. In the latter, the reaction could be enhanced by increasing the partial pressure of  $\text{SO}_3$ , which in turn increased the concentration of  $\text{V}_2\text{O}_5$ . Even with an enhanced reaction, the scandia-stabilized  $\text{ZrO}_2$  was still superior to its  $\text{Y}_2\text{O}_3$  counterpart.

Indium oxide is another oxide that Jones examined for improving the corrosion resistance of TBCs [39]. Pure  $\text{In}_2\text{O}_3$  was more resistant to reactions with sulfur and vanadium molten salts than either  $\text{Y}_2\text{O}_3$  or  $\text{Sc}_2\text{O}_3$ . A sol-gel processed  $\text{ZrO}_2$  containing 3.9 mole-percent of  $\text{In}_2\text{O}_3$

(which was sufficient to produce a material that was 100% tetragonal) was more resistant to corrosion by molten vanadium compounds than commercially available  $\text{Y}_2\text{O}_3\text{-ZrO}_2$  T/EBCs.

## 6. Summary

The addition of select oxides to stabilize the tetragonal form of zirconia at room temperature has resulted in a variety of interesting zirconia-based materials with excellent room temperature strength and toughness. The high strength and toughness is due to the transformation of the metastable t-grains. These materials are widely used in cutting tool and wear applications, and are finding increasing applications in the biomedical field. However, the selection of the stabilizing oxide and its role in controlling the  $t \rightarrow m$  transformation has also limited the usefulness of these materials.

The enhanced room temperature strength and toughness of PSZ and TZP materials unfortunately diminishes upon exposure to elevated temperatures for long times or extensive thermal cycling. Advances have not been made to maintain the room temperature properties to PSZs and TZPs viable for high-temperature structural applications such as engine components. On the other hand, thermal and environmental barrier coatings are providing excellent thermal and/or corrosion protection to metal components in some engine applications. Further improvements in the corrosion resistance of these coatings is still needed, but research currently underway indicates that coatings with improved resistance may be available soon.

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